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(54) Title: SILOXANE COMPOUNDS

(57) **Abstract:** A siloxane compound having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula -(O)_xR'- (Φ₂ wherein R' denotes a divalent hydrocarbon radical, x has a value of 0 or 1 and each Φ independently denotes a potentially substituted aryl group, and wherein both potentially substituted aryl groups are linked directly to one and the same carbon atom in the R' group, except that when only one group -(O)_xR'- Φ₂ is present in the siloxane, either the siloxane contains at least 3 silicon atoms or, where the siloxane contains only 2 silicon atoms, R' equals dimethylene has a high refractive index value. Many of these siloxane compounds have exceptionally interesting refractive indexes, including those above 1.53 or even above 1.55 which is exceptional for traditional silicones. Cosmetic composition comprising such siloxanes are also disclosed, which are preferably selected from colour cosmetic applications, lipstick, nail varnish, mascara, foundation cream, compact powders, hair colorants, hair dyes and hair conditioners.

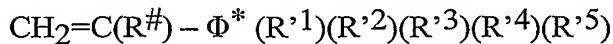
SILOXANE COMPOUNDS

[0001] The present invention relates to a siloxane compound having aryl substituents and in particular a siloxane polymer having a high refractive index. The invention relates especially to a siloxane polymer having at least one substituent containing two aryl groups substituted on one and the same carbon atom. The invention also provides in another aspect a process for making such siloxane compounds, and in yet another aspect, cosmetic skin and hair care compositions comprising siloxane compounds.

[0002] Aryl substituted siloxane compounds have been known for some time, and have been disclosed widely. Aryl substituted siloxane compounds having a relatively high refractive index are also known, and are disclosed for example in patent specifications WO 99/52965, WO 00/27348 and EP 554340.

[0003] In WO 99/52965, there is disclosed a method for the preparation of high purity polyorganosiloxanes with aralkyl function by hydrosilylation of a hydrogenpolyorganosiloxane reagent and an aromatic monovinyl compound, which method comprises the simultaneous introduction of the reagents into a reaction medium containing an inert solvent and a hydrosilylation catalyst. Examples of hydrogenpolyorganosiloxane include

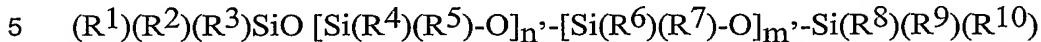
(R¹)(R²)(R³)SiO [Si(R⁴)(H)-O]_n-[Si(R⁵)(R⁶)-O]_m-Si(R⁷)(R⁸)(R⁹) or their cyclic homologues, wherein R¹ and R⁹ denote hydrogen or a C₁₋₈ alkyl radical, whereas R² to R⁸ denote independently an alkyl group having up to 8 carbon atoms, n is a number from 1 to 10, at least one of R¹ or R⁹ is hydrogen when n equals 0, and m is a number from 0 to 50. Examples of the monovinyl compound have a boiling point below 200°C and have the formula



wherein Φ* denotes an aromatic group having 6 carbon atoms, R[#] denotes hydrogen or methyl, R'¹ to R'⁵ are independently hydrogen, methyl, fluorine, chlorine or bromine.

Particular examples include styrene, alpha-methyl styrene, alpha-methyl styrene dimer and pentafluorobenzene.

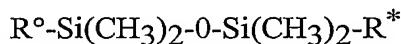
[0004] WO 00/27348 describes for example aralkyl siloxanes of the formula



wherein R¹ to R⁵ and R⁸ to R¹⁰ are each independently hydrogen, alkyl, halo alkyl, aryl or aralkyl, R⁶ and R⁷ are each independently hydrogen, alkyl, halo alkyl or aryl, n' and m' are each independently integers from 0 to 6, provided (n'+m') are ≥ 1 and provided at least one substituent group is aralkyl.

10

[0005] EP544330 describes an organosilicon compound of the general formula



wherein R[°] is selected from methyl or vinyl and R^{*} is 2-methylphenethyl. These materials are suggested as optical matching oils with a refractive index of from 1.46 to 1.51.

15

[0006] However, there is a continued need to provide siloxane compounds which have an even higher refractive index, preferably above 1.53. We have now surprisingly found that when certain aryl substituents are provided on siloxane compounds, novel materials are produced, many of which have a relatively high refractive index.

20

[0007] In Chem. Abs. 98:160766 and Chemische Berichte, 116(2), 710-23 (1983), carbanion rearrangements by intramolecular 1,ω proton shifts are described, in which the preparation of ω, ω-diphenylalkylene pentamethyl disiloxane is included, wherein the alkylene group has a minimum of 3 carbon atoms.

25

[0008] Accordingly the current invention provides a siloxane compound having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula -(O)_xR'-Φ₂ wherein R' denotes a divalent hydrocarbon radical, x has a value of 0 or 1 and each Φ independently denotes a potentially substituted aryl group, and 30 wherein both potentially substituted aryl groups are linked directly to one and the same

carbon atom in the R' group, except that when only one group $-(O)_x R' - \Phi_2$ is present in the siloxane, either the siloxane contains at least 3 silicon atoms or if only 2 silicon atoms are present, R' equals dimethylene.

5 [0009] Siloxane compounds according to the present invention have at least 2 silicon atoms, linked by an oxygen atom. They may be linear or cyclic materials, having the general formula $-[R_2SiO]_m-$ or $R_3SiO-[R_2SiO]_n-SiR_3$ wherein n denotes 0 or an integer, m denotes an integer from 3 to 20 and each R denotes a substituent, preferably selected from hydrocarbon, hydrocarbonoxy, hydroxyl or hydrogen, provided at least one silicon-bonded
10 substituent R has the general formula $-(O)_x R' - \Phi_2$ as defined above. It is possible that in addition to the groups R as defined above, some other R groups are present, which are discussed below as capping groups. It is particularly preferred that m has a value of 3 to 8, most preferably a value of 4 or 5. It is, however, most preferred that the siloxane compound is a linear siloxane where n has a value of 0 or an integer from 1 to 5, especially a value of 0
15 or 1.

[0010] The silicon-bonded substituent $-(O)_x R' - \Phi_2$ is present on at least one silicon atom of the siloxane compound. It is preferred that at least 2 silicon atoms have such substituent, and particularly preferred are siloxane compounds having on each silicon atom such substituent. It is not preferred that more than one such substituent is present on any silicon atom, and indeed it would be difficult to manufacture such compounds for reasons of steric hindrance of these relatively bulky substituents, due to the presence of aryl groups. The group R' is a divalent hydrocarbon group preferably having from 1 to 20 carbon atoms, more preferably 2 to 5, most preferably 2 or 3 carbon atoms. This hydrocarbon group is preferably saturated, and most preferably a linear alkylene group. Particular examples of suitable R' groups are dimethylene, propylene, isopropylene, butylene and isobutylene groups. It is particularly preferred that x has a value of 0, this making the substituent link to the silicon atoms via a Si-C bond. This is preferred, as some greater hydrolytic stability is believed to be achieved compared to Si-O-C bonding. Each group Φ is independently selected from
20 optionally substituted aryl groups, preferably having from 6 to 20 carbon atoms. The Φ groups include phenyl and substituted phenyls, naphthyl and substituted naphthyl, anthracyl

and phenantryl and their substituted derivatives. Most preferred however are phenyl and substituted phenyls. Suitable substituents of the aryl group include halogen, hydroxyl, alkyl, alkoxy, aryl, aralkyl and carboxyl. Examples of suitable groups Φ include phenyl, monochlorophenyl, pentachlorophenyl, tri-bromophenyl, tolyl, xylyl, xenyl, cumenyl, mesityl, 5 diphenyl, benzyl acid and benzyl alcohol. More preferred as aryl groups are those who have from 6 to 9 carbon atoms, especially unsubstituted phenyl. In the $R'-\Phi$ link, the group(s) Φ may be linked to any of the carbon atoms of the R' group, although preferably both Φ groups are linked to the terminal carbon atom of the R' group, i.e. the one furthest from the silicon atom. It is however essential that both Φ groups are substituted onto the same carbon atom of 10 the R' group. This was also found to provide the best refractive index characteristics.

[0011] Although less preferred, it is possible that only one group $-(O)_x R' - \Phi_2$ is present in the siloxane, in which case it is preferred that the siloxane contains at least 3 silicon atoms. Alternatively for such siloxanes having only one group $-(O)_x R' - \Phi_2$ where 15 the siloxane is a disiloxane R' equals dimethylene.

[0012] The other substituents on the silicon atoms of the siloxane compound may be selected from hydrogen, hydroxyl or hydrocarbyl groups or capping groups. It is preferred that the majority of these other substituents are hydrocarbyl groups, more preferably alkyl 20 groups, most preferably alkyl groups having from 1 to 8 carbon atoms. Particularly preferred are methyl groups or ethyl groups. It is most preferred that at least 80%, ideally substantially all non $-(O)_x R' - \Phi_2$ substituents are methyl groups.

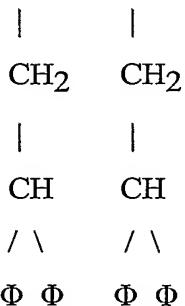
[0013] One or more capping groups may be present on the silicon atoms. They are 25 usually provided as a result of reacting any remaining silicon-bonded reactive groups, preferably Si-H groups, which have not already been substituted with the $-(O)_x R' - \Phi_2$ groups. The capping groups may be any which will react with the residual silicon-bonded reactive groups, for example aliphatic, cycloaliphatic or aralkyl alcohols, unsaturated alkene, arylene, alkarylene or aralkylene groups, which may be substituted e.g. by ether 30 functionalities. Suitable alcohols include ethanol, hexanol, benzyl alcohol, cyclohexanol, branched alkyl fatty alcohols, styrene, allyloxyethanol and vinyloxyethanol. It is preferred to

use capping agents which contain an aryl group, especially where the aim is to maintain a high refractive index value for the siloxane compound. Particularly preferred for such applications is benzyl alcohol. The capping agent may be reacted with the siloxane compound such that it forms a Si-C link, which would be achieved e.g. by hydrosilylation of 5 SiH with an alkenyl group, or a Si-OC link, which would be achieved by condensation of Si-OH or SiH with an alcohol or ether functionality, providing a side product of water or hydrogen gas.

[0014] Where the aim is not so strongly a maintaining of high refractive index, it is 10 possible to react the residual silicon-bonded reactive groups with materials which will provide the siloxane compound with additional functionality, and there is prior art which indicates what such functionality could be, especially in applications such as cosmetic 15 applications as discussed below. Suitable functionalities could include moisturizing, fragrance, colour, antimicrobial and others. It is even possible to provide capping agents which link themselves to the silicon atom of the siloxane compound by a Si-O-C linkage such that in the presence of moisture, e.g. atmospheric moisture, water, sweat, the agent could be set free through hydrolysis and perform its own function. Such hydrolysis will be more or less successful, depending on the bulk of the capping agent and its ability to allow water molecules to come near the Si-O-C linkage.

20

[0015] There is a particular interest in the material with the general formula
 $(CH_3)_2 - Si - O - Si - (CH_3)_2$



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especially where the group Φ is according to the preferred denotation indicated above, 30 preferably phenyl. This material has been found particularly effective in providing a high refractive index.

[0016] In order to provide a higher refractive index, it is preferred that either the number of aryl groups in the siloxane compound according to the invention is at least the same as the number of non-aryl containing silicon-bonded substituents. For example in the 5 particularly preferred disiloxane materials described in the previous paragraph, the ratio of aryl groups to non-aryl containing silicon-bonded substituents is 1/1 (i.e. 4 Φ groups and 4 methyl groups). Another alternative selection of the preferred siloxane compounds having a high refractive index, is those siloxane compounds in which the carbon content due to aryl groups in the siloxane compound amounts to at least 60% by weight, more preferably at least 10 70 or 75% by weight of the total carbon content of the siloxane compound. In the above exemplified preferred disiloxane material of the previous paragraph, this is 24 carbon atoms out a total of 32, or 75%.

[0017] There are a number of ways of making the novel materials according to this 15 invention. These include condensation or reaction of a number of silanes having silicon-bonded hydroxyl, halogen or alkoxy groups, wherein at least one of the silanes has at least one silicon-bonded $-(O)_xR'$ - Φ_2 substituent, as defined above. All silanes used may be ones having a silicon-bonded $-(O)_xR'$ - Φ_2 substituent, resulting in a siloxane compound having such substituents on each silicon atom in the compound. Alternatively other silanes may be 20 used, with which the silanes having at least one silicon-bonded $-(O)_xR'$ - Φ_2 substituent, are condensed or reacted. The silanes to be used require at least one condensable or reactive group, if a disiloxane compound is to be made, for example a silicon-bonded hydroxyl group or a silicon-bonded chlorine atom. Where a siloxane compound is to be made having more than two silicon atoms, the above silanes are preferably reacted with other silanes having at 25 least two condensable or reactive substituent, for example a silane with two silicon-bonded hydroxyl groups or two silicon-bonded halogen atoms, e.g. chlorine. It is particularly useful in such reaction to start from an appropriate mixture of chlorosilanes, which are readily hydrolysed and condensed according to known processes. It is also possible alternatively to start this sort of condensation reaction from oligomers, rather than silanes, or from a mixture 30 of the oligomers and silanes in which case the reactivity of all reagents is to be such that they can condense to form the desired siloxane compounds. The condensation reaction may be

carried out in the presence of suitable catalysts such as organic metal compounds such as organotin salts, titanates, or titanium chelates or complexes. Generally, these catalysts are used in amounts of between about 0.001 and 10 wt. % based on the weight of the reagent silanes or oligomers.

5

[0018] Suitable silanes or oligomers containing the preferred $-R'-\Phi_2$ substituents (i.e. $x = 0$) can be synthesized by reacting a hydrosilane, for example monochlorodimethylhydrosilane or dichloromonomethylhydrosilane, or hydrosiloxane oligomers with a compound $R''-\Phi_2$ wherein R'' is a monovalent hydrocarbon group having aliphatic unsaturation, preferably olefinic unsaturation and most preferably in the terminal carbon-carbon bond. Preferred groups R'' include C₁₋₈ groups with olefinic unsaturation, for example vinyl or allyl groups. Suitable silanes or oligomers containing $-OR'-\Phi_2$ (i.e. $x = 1$) may be prepared by condensing a group $HOR'-\Phi_2$ with a silane or oligomer having Si-OH or Si-alkoxy groups in accordance with known condensation reactions.

10

[0019] The most preferred material bis diphenylethyl tetramethyl disiloxane may accordingly be prepared from its chlorosilane analogue by reaction of 1,1-diphenylethene with dimethylchlorosilane and subsequent hydrolysis to yield the disiloxane. One benefit of this route is that the chlorosilane adduct can be purified by distillation to remove any residual traces of the platinum complex used in the hydrosilylation process, resulting in water-white materials. Very low residual monomer levels can also be achieved by selection of the distillation conditions to yield adduct of purity in excess of 99.99%.

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[0020] A more preferred synthesis method for the more preferred siloxane compounds according to the invention is the hydrosilylation of a hydrosiloxane compound with a compound of the formula $R''-\Phi_2$ group, wherein R'' is as defined above, including definition of the preferred groups R'' in the presence of a hydrosilylation catalyst.

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[0021] Accordingly the invention provides in a second aspect a process for making siloxane compounds according to the invention by reacting in the presence of a hydrosilylation catalyst a siloxane compound having at least 2 silicon atoms linked by oxygen

and having at least one silicon-bonded hydrogen atom with a compound of the formula R"- Φ_2 wherein R" is a monovalent hydrocarbon group having aliphatic unsaturation and each Φ independently denotes a potentially substituted aryl group, and wherein both potentially substituted aryl groups are linked directly to one and the same carbon atom in the R" group.

5

[0022] Siloxane compounds for use as reagent in the process according to the present invention have at least 2 silicon atoms, linked by an oxygen atom. They may be linear or cyclic materials, having the general formula -[R₂SiO]_m- or R₃SiO-[R₂SiO]_n-SiR₃ wherein n denotes an integer or 0, m denotes an integer from 3 to 20 and each R denotes a substituent, 10 preferably selected from hydrocarbon, hydroxyl or hydrogen, provided at least one silicon-bonded substituent is a hydrogen atom. It is particularly preferred that m has a value of 3 to 8, most preferably 4 or 5. It is however most preferred that the siloxane compound is a linear siloxane where n has a value of 0 or an integer, preferably from 1 to 5, especially 0 or 1. The silicon-bonded hydrogen atom is present on at least one silicon atom of the reagent siloxane 15 compound. It is preferred that at least 2 silicon atoms have a hydrogen substituent, and particularly preferred are siloxane compounds having on each silicon atom such hydrogen substituent. Although it is possible to use siloxane reagent compounds with more than one hydrogen substituent on any silicon atom, this is not preferred. It would be unlikely that more than one such hydrogen atom be reacted with the other more bulky reagent R"- Φ_2 in view of 20 steric hindrance.

[0023] The other substituents on the silicon atoms of the reagent siloxane compound may be selected from hydroxyl or hydrocarbyl groups. It is preferred that the majority of these other substituents are hydrocarbyl groups, more preferably alkyl groups, most preferably 25 linear alkyl groups having from 1 to 8 carbon atoms. Particularly preferred are methyl groups or ethyl groups. It is most preferred that substantially all non hydrogen substituents are methyl groups. There is a particular interest in the material with the general formula (CH₃)₂ - Si(H) - O - Si(H) - (CH₃)₂

as this material after reaction provides a siloxane compound with a particularly interesting

30 refractive index characteristic.

[0024] The reagent compound of the general formula $R''-\Phi_2$ has a monovalent hydrocarbon group R'' , which has aliphatic unsaturation. The group R'' is preferably a hydrocarbon group having from 1 to 20 carbon atoms, more preferably 2 to 5, most preferably 2 or 3 carbon atoms. This hydrocarbon group is preferably saturated with the exception of 5 one aliphatic unsaturation, preferably located at the terminal carbon-carbon link. Most preferably R'' is a linear alkenyl group. Particular examples of suitable R'' groups are vinyl, allyl, isopropenyl, butenyl and isobut enyl groups. Each groups Φ is independently selected from optionally substituted aryl groups, preferably having from 6 to 20 carbon atoms. Suitable substituents include halogen, hydroxyl, alkoxy, carboxyl and phenyl. More preferred 10 as aryl groups are those who have from 6 to 9 carbon atoms, especially unsubstituted phenyl groups. The groups Φ may be substituted on any of the carbon atoms of the R'' group, although preferably they are substituted on the carbon atom at the other end from the aliphatic unsaturation of the R'' group. It is however essential that both Φ groups are substituted onto 15 the same carbon atom of the R'' group. Examples of suitable compounds include 1,1-diphenylethene.

[0025] The relative proportion of the reagent siloxane compound and the compound $R''-\Phi_2$ is preferably in stoichiometric amounts based on the number of Si-H groups in the siloxane which one desires to react with the $R''-\Phi_2$ compound. It is possible to use a 20 stoichiometric excess of the compound $R''-\Phi_2$, but in such cases, it is preferred to remove the unreacted compounds from the reaction product if high purity is preferred. Any unreacted Si-H groups remaining in the siloxane compound reaction product are then preferably further reacted with a capping agent, as discussed above under the first aspect of the invention.

25 [0026] Hydrosilylation catalysts are known in the art and have been described in a number of publications. They are generally Group VIII transition metal catalysts, as described e.g. in US patents 3,715,334 and 3,814,730. Suitable hydrosilylation catalysts include complexes or compounds of group VIII metals, for example, platinum, ruthenium, rhodium, palladium, osmium and indium. Preferred catalysts are platinum compounds or 30 complexes including chloroplatinic acid, platinum acetylacetone, complexes of platinous halides with unsaturated compounds, for example, ethylene, propylene, organovinylsiloxanes

and styrene, hexamethyldiplatinum, $\text{PtCl}_2\text{PtCl}_3$ and $\text{Pt}(\text{CN})_3$. Alternatively the catalyst may be a rhodium complex, for example, $\text{RhCl}_3(\text{Bu}_2\text{S})_3$. Generally, these catalysts are used in amounts of between about 0.0001 and 10 wt. % based on the weight of the reagent siloxane polymer. Hydrosilylation reactions are generally carried out at a temperature of from 40°C up
5 to 200°C, preferably 80°C to 150°C, and at normal atmospheric pressure, although both lower and higher pressures can be applied. Although the hydrosilylation catalyst are designed to catalyse a hydrosilylation reaction, they can also be active to catalyse condensation reactions, such as those described above for the capping agents.

10 [0027] Many of the siloxane compounds according to the present invention are found to have exceptionally interesting refractive indexes, especially the more preferred compounds, where refractive indices above 1.53 are not exceptional, even values above 1.55 can be achieved consistently. Such refractive indices are rarely achieved for siloxane materials, and some of the values seen were never previously achieved for siloxane compounds. It follows
15 that these compounds have a very wide potential use in applications where refractive index values are important. Such uses include coating applications, additives for construction materials or decorative materials, for example paints and varnishes, cosmetic applications, in particular antiperspirant applications, hair care applications, including conditioning, colouring and dyeing applications and skin care applications, including moisturising, colouring,
20 protecting and general treatment applications. They are particularly interesting in those cosmetic applications where appearance becomes important, such as shine or colouring, for example colour cosmetics, lipstick, eye shadow, mascara, nail varnish, hair colouring and hair dyeing. There is an extra benefit in the use of such siloxane compounds, because of the additional traditional benefits of siloxanes which can also be imparted to the treated hair or
25 skin. Benefits include for example the improved feel on skin, improved gloss, softening and conditioning.

30 [0028] The siloxane compounds according to the first aspect of the invention, and even those which do not have both Φ groups on a single carbon atom or those having only one $-(\text{O})_x \text{R}'-\Phi_2$ group per molecule, regardless of the number of silicon atoms or the R' group, have demonstrated benefits in many applications, significantly in personal care

applications where the high refractive index can offer masking of antiperspirant salts in under arm products. They have demonstrated excellent compatibility with a very wide range of organic chemicals (including hydrocarbon oils, esters, alcohols, waxes and silicones), in particular they have shown excellent compatibility with castor oil and perfumes and essential 5 oils, in comparison to many other phenyl containing silicones. Good compatibility with gellants such as silicone polyamides for use for example in lip-gloss was also observed. They have the ability to impart shine or enhanced gloss on skin and may find benefit in skin applications such as lipsticks. It was surprising to find also a benefit in the consistency and hardness of some cosmetic sticks, such as lipsticks. It retains the good aesthetics and feel of 10 more traditional silicones imparting a luxurious "feel" on the skin. It has interestingly also shown excellent dispersion properties for pigments such as mica.

[0029] A relatively low viscosity coupled with high refractive index, high purity and excellent compatibility with personal care ingredients have been demonstrated, which 15 benefits are based on the unique composition of many of these novel materials. Many other high aryl containing siloxane compounds tend to be either solid at room temperature or have too low a refractive index.

[0030] Accordingly the invention provides in another aspect a cosmetic skin, body or 20 hair care composition comprising a siloxane compound having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula $-(O)_x R' - \Phi_2$ wherein R' denotes a divalent hydrocarbon radical and Φ denotes a potentially substituted aryl group. It is particularly preferred that both potentially substituted aryl groups are linked directly to one and the same carbon atom in the R' group. Particularly preferred are those 25 cosmetic skin, body or hair care compositions comprising siloxane compounds according to the first invention, i.e. those having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula $-(O)_x R' - \Phi_2$ wherein R' denotes a divalent hydrocarbon radical, x has a value of 0 or 1 and each Φ independently denotes a potentially substituted aryl group, and wherein both potentially substituted aryl groups are linked directly 30 to one and the same carbon atom in the R' group, except that when only one group $-(O)_x R' -$

Φ_2 is present in the siloxane, either the siloxane contains at least 3 silicon atoms or if only 2 silicon atoms are present, R' equals dimethylene

[0031] It is particularly preferred that the skin care composition is selected from 5 colour cosmetic compositions, and in particular lipstick, nail varnish, foundation creams, compact powders and mascara. With regard to hair care compositions, it is preferred that the application intended is selected from hair colouring or hair dyeing applications and hair conditioners.

10 [0032] Skin, body and hair care compositions according to this aspect of the invention would incorporate siloxane compounds in an amount of from 0.1 up to 50% by weight of the total composition, preferably from 1 to 10% by weight, more preferably 3 to 7% by weight. They could be incorporated as a pure material, or included in an emulsion or dispersion. They may be applied to a powder or mixed in with liquid or paste like materials.

15 [0033] In order to further clarify the invention, a number of examples are provided, which are not limitative. In the examples, all percentages and parts or proportions are by weight, unless otherwise indicated and all viscosities are kinematic viscosity measured at 25°C and atmospheric pressure. Refractive Index measurements were made on undiluted 20 materials, at 25°C. For examples 1 to 6 and 9, they were measured using an Abbe Refractometer Mk II Plus, supplied by Fisher Scientific. For examples 7 and 8 and for the comparative Example, they were measured using a KEM Refractometer RA-510, supplied by Kyoto Electronics.

25 Example 1

[0034] To a clean, dry flask fitted with agitator, water condenser and thermocouple, blanketed with inert gas was added 500g (2.77 moles) of 1,1-diphenylethene and 200g (1.49 moles) tetramethyldisiloxane. The mixture was warmed to 35°C and a quantity of a platinum 30 based catalyst, which resulted in a platinum concentration of 25ppm based on the total mixture, was added. A slight exotherm to 39°C and a slight colour change from colourless to

pale orange were noticed. The mixture was slowly heated over 60 minutes until reflux was achieved at 88°C, and reflux was then maintained, the temperature rising to 105°C over the next 4 hrs. After a further 2 to 3 hours, the temperature was raised to 125°C for a further 16 to 24 hours. The reaction mixture was periodically sampled and analysed by gas-liquid chromatography (gc) and the reduction in unreacted tetramethyldisiloxane and 1,1-diphenylethene was followed, showing a corresponding increase in reaction products with time. The principal reaction product was the addition product of 1,1-diphenylethene and the silicon hydride. Due to the stoichiometric excess of SiH (2 SiH groups per molecule) over unsaturated carbon, trace residues of 1,1-diphenylethene remained together with a significant concentration of the mono-substituted disiloxane. This was further reacted at 125°C with 20g (0.085 moles) of alpha methyl styrene dimer. This reacted with substantially all remaining SiH moieties in the disiloxane over a period of 16 to 24 hours. The resulting di-substituted siloxane was shown by gc analysis to be in the presence of 124 ppm residual 1,1-diphenylethene and 104 ppm residual alpha methylstyrene dimer. The physical properties of the siloxane were measured as follows: viscosity: 155.2 mm²s⁻¹; refractive index at 25°C: 1.5613; residual SiH: 5 ppm.

Example 2

20 [0035] To a clean dry flask fitted with agitator, water condenser, thermocouple and blanketed with nitrogen was added 100g (0.55 moles) of 1,1-diphenylethene and 40g (0.29 moles) of tetramethyldisiloxane and sufficient quantity of a platinum complex to give a platinum concentration in the reagent mixture of 25 ppm. Heating was applied and at 100°C a slight reflux took place, which lasted for 2-3 hours. The temperature was raised over the 25 next 5 hour period to 128°C and was held for a further 24 hours. The resultant mixture was analysed by gc to yield a material with the following properties: viscosity: 130.7 mm²s⁻¹; refractive index: 1.5599; residual SiH content: 4.5 ppm; residual 1,1-diphenylethene content: 184 ppm.

Example 3

[0036] To a clean dry flask fitted with agitator, water condenser, thermocouple and blanketed with nitrogen was added 500g (2.77 moles) of 1,1-diphenylethene and 200g (1.49 moles) of tetramethyldisiloxane. The mixture was warmed to 35°C and sufficient platinum complex added to generate a platinum concentration of 25 ppm. There was an immediate slight exotherm to 39°C coupled with a change in colour to a pale orange. Further heat was applied to raise the temperature to 85°C where the mixture started to reflux gently. The temperature was gradually increased over the next 8 hours to 105.4°C, where the reaction mixture was held for 16 hrs, then increased to 125.2°C and again held for approx 24 hours.

Periodic sampling of the mixture for analysis by gc showed the gradual consumption of all tetramethyldisiloxane, with only a trace of unreacted 1,1-diphenylethene and about 5% of mono substituted disiloxane left. The mixture was allowed to cool to room temperature and 14g (0.13 moles), corresponding to an addition level of 2 % of benzyl alcohol was added.

15 The mixture was heated to 125°C and held for 16 hours after which all but a trace of the mono-substituted disiloxane remained, as observed by gc. The resultant material was filtered through a 5 micron filter to yield a pale straw liquid, having a viscosity of 135.8 mm²s⁻¹, a refractive index of 1.5604, a residual SiH content of 5ppm and a residual 1,1-diphenylethene level of 10 ppm.

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Examples 4-6

[0037] The process of Example 3 was repeated, but the benzyl alcohol was replaced with 1-octene, allyloxy ethanol, and geraniol respectively. The resulting siloxane compounds 25 only reduced the refractive index by less than 0.05 units (i.e. retaining final refractive index above 1. 54).

Example 7

30 [0038] To a clean, dry flask fitted with water condenser, agitator and blanketed with dry inert gas was added 9.4g (0.1 mole) of dimethylchlorosilane and sufficient platinum

complex to give a 25ppm concentration of platinum in the reaction mixture. The silane was heated to 35°C, at which temperature there was a gentle reflux and to it was added drop-wise over 75 minutes 21.6g (0.12 moles) of 1,1-diphenylethene. At the end of the addition the reactor temperature was 45°C with only a slight reflux, this was maintained for a further 4 to 5 hours. Analysis by gc showed complete conversion of the silane to the diphenylethyl adduct. Hydrolysis of this product yielded a material with a viscosity of 66mm²s⁻¹ and a refractive index of 1.5602.

Example 8

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[0039] To a clean, dry flask fitted with water condenser, agitator and blanketed with dry inert gas was added 0.1 mole of methyldichlorosilane and sufficient platinum complex to give a 25ppm concentration of platinum in the reaction mixture. The silane was heated to 35°C, at which temperature there was a gentle reflux and to it was added dropwise over 75 minutes 0.12 moles of 1,1-diphenylethene. At the end of the addition the reactor temperature was 45°C with only a slight reflux, this was maintained for a further 4 to 8 hours. Analysis by gc showed complete conversion of the silane to the diphenylethyl adduct. This product was then mixed in a ratio of 1:3 to the prehydrolysed silane of Example 7, and the mixture was hydrolysed in a water/toluene mixture with sodium bicarbonate to mop up the HCl produced. After removal of the solvents and by-products, a mixture in a 1:1 weight ratio was obtained of the disiloxane of Example 7 and a trisiloxane compound having on each silicon atom a diphenylethylene substituent with a viscosity of 66mm²s⁻¹ and a refractive index of 1.572.

25 Example 9

[0040] To a clean, dry flask fitted with water condenser, agitator and blanketed with inert gas was added 16.3g (0.11 moles) of pentamethyldisiloxane and 25g (0.14 moles) of 1,1-diphenylethene. To this was added sufficient platinum complex to achieve a platinum concentration of 25 ppm. The mixture was heated to 88°C where a slight reflux was observed. Heating continued over the next 8 hours when the temperature rose to 98°C. A

sample of the mixture was analysed by gc and shown to contain no unreacted siloxane but a residual 1,1-diphenylethene content of approximately 20wt%. The viscosity was measured at 9.9 mm²s⁻¹ and a refractive index of 1.5600

5 Comparative Example

[0041] To a clean dry flask fitted with agitator, water condenser, thermocouple and blanketed with nitrogen was added 220g of tetramethyldisiloxane, 680g (2.89 moles) of alpha methylstyrene dimer and an appropriate quantity of a platinum catalyst to give a platinum 10 concentration of 50ppm. The mixture was slowly heated to 85°C, where it started to reflux. Heat was continually applied and over the next 6 hours the temperature gradually rose to 108°C, where it was left for a further 24 hours. Periodic samples were taken and analysed by gc. At the end of this time the mixture was shown to consist of a trace of unreacted 15 tetramethyldisiloxane, a slight trace of unreacted alpha-methyl styrene dimer and a significant portion of monosubstituted disiloxane. A further 5 ppm of Pt was added and heating continued to 120°C for a further 24 hours. The resultant product was shown to contain 20 ppm residual SiH, 4528 ppm alpha-methylstyrene dimer having a viscosity of 109.3 mm²s⁻¹ and a refractive index of 1.5372.

20 Example 10

[0042] A lipstick was prepared by making a pigment formulation of 5 parts of Covasil® TiO₂, 17.5 parts of Covasil® red W3801 and 77.5 parts of decamethyl cyclosiloxane. 27 parts of this pigment formulation was then formulated with 8 parts 25 Novol®, 2 parts avocado oil, 9 parts lanolin oil, 4 parts petrolatum, 5 parts of a siloxane having methyl and C16 alkyl substituents on most silicon atoms, 25 parts of Eutanol® G, 11 parts of candellila wax, 5 parts of the siloxane material of Example 2 and 4 parts of white ozokerite wax. The resulting lipstick was tested by a panel of experts and found to be easy to apply and retain a very high gloss, even after prolonged time.

Example 11

[0043] A lip gloss product was made using 16.5 parts of Dow Corning® 2-8178 silicone polyamide gellant, 32.96 parts of decamethyl cyclopentasiloxane, 22.42 parts of 5 isopropyl myristate, 22.42 parts of Crodamol® GTCC, 0.2 parts of a pigment mix and 5.5 parts of the siloxane compound of Example 2. The finished product was tested by a panel of experts and was shown to give a good level of gloss when applied.

CLAIMS

1. A siloxane compound having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula $-(O)_x R' - \Phi_2$ wherein R' denotes a divalent hydrocarbon radical, x has a value of 0 or 1 and each Φ independently denotes a potentially substituted aryl group, and wherein both potentially substituted aryl groups are linked directly to one and the same carbon atom in the R' group, except that when only one group $-(O)_x R' - \Phi_2$ is present in the siloxane, either the siloxane contains at least 3 silicon atoms or, where the siloxane contains only 2 silicon atoms, R' equals dimethylene.
2. A siloxane compound according to Claim 1, wherein the siloxane compound is a disiloxane or a trisiloxane compound.
3. A siloxane compound as claimed in Claim 1 or 2, wherein a substituent $-(O)_x R' - \Phi_2$ is present on more than one silicon atoms.
4. A siloxane compound as claimed in anyone of the preceding claims, wherein R' is a divalent hydrocarbon radical having 2 or 3 carbon atoms.
5. A siloxane compound as claimed in anyone of the preceding claims, where in addition to the silicon-bonded $-(O)_x R' - \Phi_2$ substituent(s), silicon-bonded alkyl groups having from 1 to 8 carbon atoms are present.
6. A siloxane compound of the formula
$$(CH_3)_2 - Si - O - Si - (CH_3)_2$$
$$\begin{array}{c} | & | \\ CH_2 & CH_2 \\ | & | \\ CH\Phi_2 & CH\Phi_2 \end{array}$$
wherein Φ is as defined above.

7. A siloxane compound according to any of the preceding claims, wherein each Φ denotes a group C_6H_5 .
8. A process for making siloxane compounds according to any of the preceding claims, provided x equals 0, by reacting in the presence of a hydrosilylation catalyst a siloxane compound having at least 2 silicon atoms linked by oxygen and having at least one silicon-bonded hydrogen atom with a compound of the formula $R''-\Phi_2$ wherein R'' is a monovalent hydrocarbon group having aliphatic unsaturation and each Φ denotes independently a potentially substituted aryl group, and wherein both potentially substituted aryl groups are linked directly to one and the same carbon atom in the R'' group
9. A cosmetic composition for use in skin or hair care applications, comprising a siloxane compound having at least 2 silicon atoms linked by oxygen and at least one silicon-bonded substituent of the general formula $-(O)_x R'-\Phi_2$, wherein R' denotes a divalent hydrocarbon radical, x has a value of 0 or 1 and each Φ independently denotes a potentially substituted aryl group.
10. A cosmetic composition according to Claim 9, wherein both potentially substituted aryl groups of each $-(O)_x R'-\Phi_2$ substituent in the siloxane compound are linked directly to one and the same carbon atom in the R' group.
11. A cosmetic composition according to Claim 9 or 10, which comprises from 0.1 to 50% by weight of the siloxane compound.
12. A cosmetic composition according to anyone of Claims 9 to 11, which is selected from colour cosmetic compositions, lipstick, nail varnish, mascara, foundation cream, compact powders, hair colorants, hair dyes and hair conditioners.